Catalysis Communications 56 (2014) 148–152

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

New non-metallic mesoporous SBA-15 catalyst with high selectivity for the gas-phase oxidation of cyclohexylamine to cyclohexanone oxime

Wenzhou Zhong [a,b], Liqiu Mao [b], Wenjun Yi [b], Steven Robert Kirk [b], Dulin Yin [b,*], Anmin Zheng [c], Hean Luo [a,*]

[a] College of Chemical Engineering, Xiangtan University, Xiangtan 411105, PR China
[b] National & Local United Engineering Laboratory for New Petrochemical Materials & Fine Utilization of Resources, Hunan Normal University, Changsha 410081, PR China
[c] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics Chinese Academia of Sciences, Wuhan 430071, PR China

ARTICLE INFO

Article history:
Received 5 February 2014
Received in revised form 21 April 2014
Accepted 30 June 2014
Available online 8 July 2014

Keywords:
SBA-15
Cyclohexylamine
Cyclohexanone oxime
Selective oxidation

ABSTRACT

Non-metallic mesoporous SBA-15 is firstly used for the gas-phase selective oxidation of cyclohexylamine to cyclohexanone oxime with air and exhibits the best performance among the investigated silica catalysts. The experimental results show that the catalytic activity is strongly dependent on the pore diameter of SBA-15. By combining catalytic performance experiments with the monitoring of catalyst transformations using themogravimetric analyses, N_2-physisorption, and solid-state ^{29}Si MAS NMR spectra, we show that the surface silanols play important roles to form a catalytically active carbon species, which is believed to be favorable to the activation of molecular oxygen. The carbon species formed are also studied by IR-spectroscopy, coke analysis by a catalyst dissolution/extraction protocol and elemental analyses.

1. Introduction

The selective oxidation of amine is an important chemical transformation in the synthesis of fine chemicals, medicines, and biologically active compounds [1]. Selective oxidation of cyclohexylamine is one such reaction, one of the products of which viz. cyclohexanone oxime is a valuable intermediate in the manufacture of nylon-6 [2]. Several oxidation procedures using oxidants such as some salts of Cr^{VI} or Mn^{VII} [3], alkylhydroperoxide [4] and hydrogen peroxide [5] have been reported in the presence of transition metal compounds as catalysts for this reaction. Currently, a catalytic system using air/molecular oxygen as a sole oxidant has been desired in view of green chemistry. For example, diphenyl-2-picrylhydrazyl and tungstated alumina are found to be good catalysts for cyclohexylamine selective oxidation [6]. Gold nanoparticles supported on titania are also known to be effective for oxidation of cyclohexylamine [7]. The environmental limitation for the usage of solvent and the catalyst separation is, however, still one of the important remaining problems in the liquid systems. To overcome these problems and make the processes "greener", heterogeneously catalyzed reactions for gas-phase oxidation are under investigation. Most of these solid catalysts are Al_2O_3-based catalysts such as WO_3/Al_2O_3 [8] and $H_4[Si(W_3O_{10})_4/Al_2O_3$ [9], which exhibit moderate deactivation. In particular, the sensitivity of cyclohexylamine to metal catalysts leads to relatively low selectivity for oxime.

Silica is generally considered as catalytically inactive solid. Some silica-based materials have been already proven; however, to be attractive alternatives to conventional metal-based catalysts for several oxidation reactions, for example, ammoximation of cyclohexanone [10], oxidation of methane [11], butane [12], carbon oxide [13] or photo-oxidation processes [14]. They have attracted much interest for their extraordinary catalytic performance, exhibiting an opportunity to develop new catalysts for more economic and environmentally friendly processes. Importantly, the excellent catalytic performances of non-metallic SiO_2 materials are linked to their manifold structures and surface chemistry [15,16]. Mesoporous SBA-15 has attracted a great deal of attention for applications in the fields of adsorption and heterogeneous catalysis, due to its well-defined hexagonal structure and high hydrothermal stability [17]. In catalysis, many efforts have been focused on metal-supported SBA-15 for heterogeneous catalytic oxidation reactions. However, in the literature there are also some announcements concerning the activity of SBA-15 silica in the oxidation processes [18]. Herein, we report a highly selective and efficient catalytic method for the oxidation of cyclohexylamine to oxime by employing mesoporous SBA-15 itself acting as a metal-free catalyst with air as the terminal.

2. Experimental

2.1. Catalyst preparation

The mesoporous SBA-15 materials were synthesized by a template method as described in the previous paper [19]. For a typical synthesis, 4.0 g of P_{123} [$EO_{20}PO_{70}EO_{20}$, poly(ethyleneglycol)-

---

* Corresponding authors. Tel./fax: +86 731 88872531.
E-mail addresses: dulinyin@126.com (D. Yin), hluo@xtu.edu.cn (H. Luo).

http://dx.doi.org/10.1016/j.catcom.2014.06.030
1566-7367/

block-poly(propyleneglycol)-block-poly(ethyleneglycol), average molecular weight = 5800, Aldrich] was dissolved in 90 ml deionized water at ambient temperature under violent stirring. Subsequently, 60 ml of 4 mol l^{-1} HCl (CR, Sinophar) was introduced with continuous stirring. 9.8 ml of tetraethyl orthosilicate (CR, Damao) was added dropwise into the former solution at 40 °C. After being stirred continuously for 24 h, the mixture was transferred to a Teflon-lined stainless steel autoclave and placed in an oven at 100 °C (aging temperature) for 24 h. The precipitate was in turn filtered, washed with deionized water, and dried at 80 °C overnight. The obtained powders were finally heated up to 550 °C at a ramp rate of 1 °C/min and calcined at this temperature in air for 8 h. To investigate the effect of the structural properties on the catalytic performance, the preparation was conducted with different aging temperatures (60, 80, 100, 110, 120 and 140 °C) and the addition of a swelling agent (trimethylbenzene) according to [20], which allow one to change the pore diameter and pore volume. For comparison, the other mesoporous silicas MCM-41, SBA-3 and HMS were also prepared according to [21–23], respectively. Grance gel was supplied by Aldrich.

2.2. Catalyst characterization

The nitrogen adsorption–desorption measurements were carried out at −196 °C on a Tristar 3000 sorptometer. Themogravimetric analyses (TGA) were performed with TA Instruments equipment from 50 to 800 °C operating at 10 °C/min under airflow. Solid-state ^{29}Si MAS NMR spectra were recorded on a Varian Infinitypuls at a Larmor frequency of 121.35 MHz. The chemical shifts for the ^{29}Si resonance were referred to tetramethylsilane. All solid-state NMR experiments were carried out with a spinning rate of 8 kHz and silanol concentrations were calculated by dividing the molar fraction of the respective silicon species by the molar weight of the sample (determined as sum of molar weights and fractions of the different silicon species). Fourier transformation infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm^{-1}. Samples were dehydrated at 200 °C for 6 h under nitrogen and ground with KBr in the ratio 1:150 and pressed into thin wafers. Elemental analyses (C, H, N) were performed using a Carlo Erba CE Instruments EA 1110.

In order to determine the nature of the carbon species, ca. 15 mg of the spent SBA-15 was dissolved in 1 cm^3 of a concentrated HF aqueous solution (40%, Sinophar) at room temperature. Subsequently, 4 cm^3 of CH_2Cl_2 was added to extract the soluble carbon material which, after its separation from the aqueous phase, was analyzed by HPLC–MS (Agilent 1260/6120).

2.3. Catalyst testing

The vapor phase oxidation of cyclohexylamine was carried out in a fixed bed vertical downward flow glass reactor of internal diameter 2 cm. About 1.2 g of a catalyst was placed at the center of the reactor supported on either side with a thin layer of quartz wool and ceramic beads. The weight hourly space velocity (WHSV) of cyclohexylamine was 43.2 h^{-1}. The oxidation was performed by air at atmospheric pressure and at a temperature of 190 °C. The flow rate of gases was 70 cm^3 min^{-1}. The reactant was fed into the reactor using a syringe infusion pump. The products, collected in the receiver flask, were analyzed in a gas chromatograph (Agilent 6890N) equipped with a DB-5 capillary column (30 m) and a flame ionization detector using naphthalene as an internal standard. The components of the gas phase were analyzed by gas chromatography with a TCD detector. The products were identified by GC–MS (SHIMADZU, QP2010 PLUS) and by comparison with commercially pure products. The conversion of cyclohexylamine and selectivity of cyclohexanone oxime were calculated using the following formulas (Eqs. (1) and (2)). All raw materials and products were established carbon mass balances.

Table 1
Physicochemical properties and catalytic performances of various silicas.[a]

Sample	D[b] (nm)	S_{BET}[b] (m^2/g)	V_p[b] (cm^3/g)	Conversion (%)	Selectivity (%)
Silica gel	9.25	314	0.86	3.7	61.3
SBA-15	6.13	783	1.33	11.2	96.6
MCM-41	3.32	736	0.69	1.6	93.4
SBA-3	2.86	594	0.33	0.15	98.1
HMS	3.01	785	0.45	0.24	96.4
Null	–	–	–	–	–

[a] Reaction conditions: space velocity 43.2 h^{-1}; air, 70 cm^{-3}/min; temperature, 190 °C; time, 11 h.

[b] D: pore size; S_{BET}: surface area calculated by BET method; V_p: pore volume.

$$\text{Conversion of cyclohexylamine }(\%) = \frac{[\text{the amount (mol) of starting cyclohexylamine}] - [\text{the amount (mol) of cyclohexylamine recovered}]}{[\text{the amount (mol) of starting cyclohexylamine}]} \times 100\% \tag{1}$$

$$\text{Selectivity of cyclohexanone oxime}(\%) = \frac{[\text{the amount (mol) of cyclohexanone oxime}]}{[\text{the amount (mol) of starting cyclohexylamine}] - [\text{the amount (mol of cyclohexylamine recovered)}]} \times 100\% \tag{2}$$

3. Result and discussion

3.1. Catalytic performance of various silica catalysts

Catalytic performances of various silica materials are summarized in Table 1. As expected, the blank experiment without any catalyst gives no cyclohexylamine conversion as a result of the catalytic oxidation reaction. High activity is obtained over SBA-15 to yield a conversion of 11.2% (with 96.6% cyclohexanone oxime selectivity), which is remarkably higher than those on the other silica catalysts. When silica gel is applied to the reaction, the selectivity for the oxidation is as low as 61.3%, which is the lower compared with the other mesoporous silica catalysts (>93%). This great difference between the catalytic activities of SBA-15 and the other silica catalysts is very interesting considering that the various walls of mesoporous silica and silica gel are all made of amorphous silica. What is the cause of this great difference? First, we compare the specific surface area, pore volume size and pore size distribution of various silica catalysts obtained by using N_2-physisorption. As shown in Table 1, the commercial silica gel with the lower specific surface area has higher catalytic activity than those of mesoporous silica (MCM-41, HMS, SBA-3). This indicates that the specific surface area is not the most important factor which determines the oxidation activity of silica. On the other hand, both SBA-15 and silica gel have relatively high pore volume with a wide pore size distribution centered above 6 nm and the higher conversions are achieved, indicating that pore volume size is more responsible for the formation of oxime. Next, we studied the dependence of catalytic activity on the pore size of the SBA-15 samples, as shown in Fig. 1. Surprisingly, catalytic activity is strongly dependent on the pore diameter of the catalyst and is maximized at around 6.1 nm. Smaller or larger pores are not suitable for the catalytic oxidation of cyclohexylamine, which can not be only associated that the shape selective catalysis may be involved in this process. In the present reaction, the diameter of cyclohexylamine is 0.79 nm (the distance between hydrogen and the most distant hydrogen is 0.59 nm; the van der Waals radius of hydrogen is 0.10 nm) and that of the product should be 0.86 nm, while the most appropriate pore diameter for the catalyst is approximately 6.1 nm. The phenomenon may be accounted for by structural characteristics of SBA-15. First, some synergistic effect may be involved at larger pores, but for pores less than 4 nm in size, diffusion

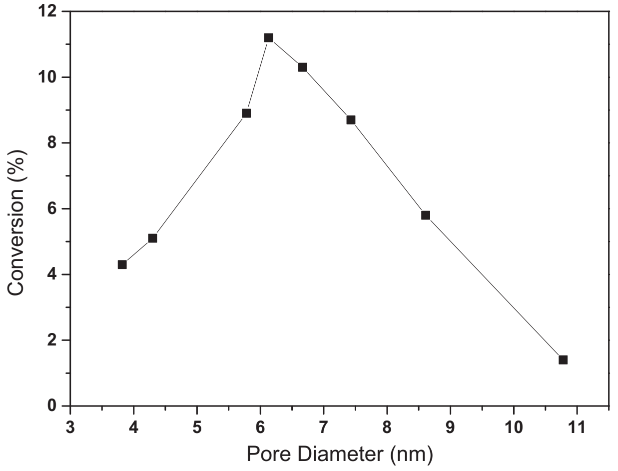
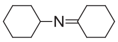
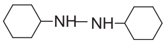


Fig. 1. The dependence of catalytic activity on the pore size of the SBA-15 samples.

effects may determine the rate. Second, the catayst may be rapidly deactivated by the deposition of carbon species less than 4 nm in size, which block the reactants from accessing the active sites. The third possible explanation is that all of the surface hydroxyl groups on the pore will point to the center of each pore, and thus they could work as a group. From these results, we can conclude that SBA-15 served as a catalyst for the vapor-phase oxidation by taking advantage of its specific structure (like key and lock).

3.2. Correlation between catalytic performance and structural characteristics of SBA-15

Fig. 2A presents the evolution of the catalytic behavior with the time on stream over SBA-15 catalyst. We found that the conversion to cyclohexanone oxime was zero in the beginning of the reaction. After 1 h, the conversion and the oxime selectivity increased progressively, indicating a process of activation of the catalyst. Along with the reaction time of 11 h, 96.6% cyclohexanone oxime selectivity was achieved at a conversion of 11.2%, and then kept approximately constant for some hours. After that, the activity progressively decreased due to a deactivation phenomenon, which might be attributed to the blocking of part of the mesopore, blocking the reactants from accessing the active sites. However, the observed oxime selectivity slightly decreased with the time on stream. This could be due to the fact that the formed oxime was hydrolyzed by steam that was produced during oxidation of cyclohexylamine and converted to cyclohexanone. Moreover, traces of cyclohexanone, aniline, phenol, cyclohexanol, cyclohexene, nitrocyclohexane,  and  were detected in the liquid phase products. Some deep oxidation products such as CO_2 and CO were not detected in the gas phase when the reaction temperature was over 190 °C.

The change in the SBA-15 structural characteristics during the reaction is monitored using N_2-physisorption, themogravimetric analyses (TGA) and solid-state ^{29}Si MAS NMR spectra. The catalysts sampled from the reaction are denoted by SBA-15/xh, where x indicates the reaction time (h). First, we investigate the relationship between the amount of carbon species present on the catalyst and its catalytic activity. During the reaction, a weight loss at about 350 °C, which can be observed by TG-DTA, gradually form, and their number increases, as evidenced by a color change of the sampled catalysts due to the increase in the surface amount of carbon species (Fig. S1). Approximately 10.7%, 22.1%, 37.6% and 40.9% carbon species content are estimated in Table 2, indicating that carbon species formation occurs very quickly at the beginning and then slowly increases with time on stream. Meanwhile, the total surface area and pore volume dramatically reduce from 783 m^2/g and 1.33 cm^3/g to 80 m^2/g and 0.14 cm^3/g, respectively, with increasing reaction time from 1 to 6 h (Table 2). However, a slight decrease in the total surface area and total pore volume after 6 h reaction is also noticed. These results are attributed to the change of catalyst surface covered by the amount of carbon species.

As seen from the catalytic behavior of cyclohexylamine oxidation (Fig. 2A), N_2-physisorption and TGA data, at the beginning the formation of a sufficient number of carbon species is accompanied by the appearance of highly catalytic activity, which indicates that such carbon species are active in cyclohexylamine oxidation. Moreover, the data do not display a direct correlation between activity and surface area. We believe that formed carbon species are responsible for O_2 activation, which is similar to ammoximation of cyclohexanone in the gas phase [16]. The introduction of small amounts of carbon species in SBA-15 using phenolic resin as carbon precursors serves to activate the original catalyst. The absence of an induction period for supported carbon species in SBA-15 supports this conclusion (Fig. 2B).

Next, the change of the silanols in the samples is assessed by ^{29}Si MAS NMR technology. As shown in Fig. S2, the spectra of the three samples display three resonances centered at ca. −110, −100, and −92 ppm that can be assigned, respectively, to $Si(OSi)_4$ [Q_4], $HOSi(OSi)_3$ [Q_3], and $(HO)_2Si(OSi)_2$ [Q_2] environments around silicon. As such, the measured contents of silanols are 6.2, 1.8, and 2.9 mmol/g of SiO_2 for SBA-15/0 h, SBA-15/6 h, and SBA-15/11 h, respectively. Interestingly, the content of silanols for SBA-15/6 h is significantly lower than the corresponding value based on the fresh SBA-15, indicating that the silanol groups in

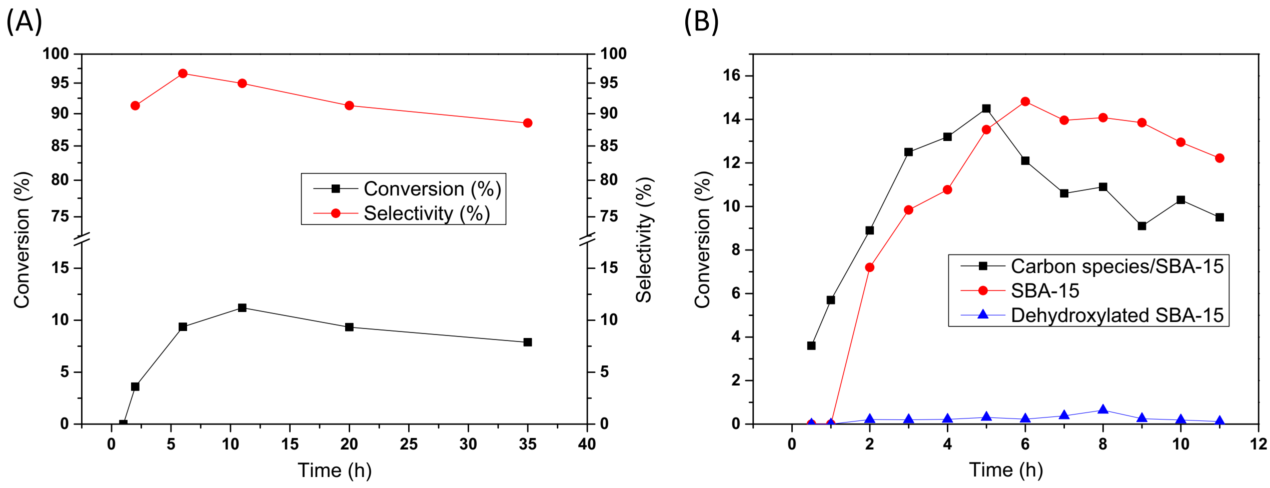


Fig. 2. SBA-15 samples (A) and modified SBA-15 samples (B) reaction time in hours. Reaction conditions: space velocity 43.2 h^{-1}; air, 70 cm^{-3}/min; temperature, 190 °C.

Table 2
Main characteristics of the SBA-15/xh.

Sample	D[a] (nm)	S_{BET}[a] (m^2/g)	V_p[a] (cm^3/g)	Total carbon[b] species (wt.%)	Total silanol[c] (mmol/g)	^{29}Si chemical environment (%)[c]		
						Q_2	Q_3	Q_4
SBA-15/0 h	6.13	783	1.33	–	6.2	4	32	64
SBA-15/1 h	6.26	608	1.15	10.7	–	–	–	–
SBA-15/2 h	6.00	324	0.64	22.1	–	–	–	–
SBA-15/6 h	6.73	80.1	0.14	37.6	1.8	1	13	86
SBA-15/11 h	6.91	65.8	0.15	40.9	2.9	2	19	79

[a] D: pore size; S_{BET}: surface area calculated by BET method; V_p: pore volume.
[b] Estimated from weight loss in TG curve.
[c] Quantified by ^{29}Si MAS NMR.

the samples take part in reacting with the reactants to form carbon species. At the same time, the reaction with silanol groups (Q_2 and Q_3), produces weak signals in the spectrum and a signal at 101 ppm is significantly intense due to the formation of Si-O-Si in the SBA-15/6 h. As was noted in Table 2, a different trend is observed for the SBA-15/11 h. One can see that the intensities for the Q_2 and Q_3 group significantly increase and for the Q_4 significantly decrease, respectively. Due to the hydrolysis of Si–O–Si groups in the surface structure of SBA-15 with the steam produced by oxidation of cyclohexylamine, these groups are converted to new silanol groups as new active sites. Moreover, in order to investigate the silanol groups as active sites, the surface-OHs of SBA-15 are dehydroxylated using a trimethylsilylation agent and the formation of oxime decreases, which supports this conclusion (Fig. 2B).

3.3. Analysis of carbon species formed as a function of the time on stream

To obtain further information on the retained carbon species and their interaction with the SBA-15 framework, FTIR spectroscopy was performed on the fresh and spent samples. The results are reported in Fig. 3. The band related to H-bonds in silanols decreases greatly in intensity and shifts to 3357 cm^{-1} (NH stretchings), indicating some heterogeneity in the H-bonded complexes and the band at 1542, 1513, 1457 and 1430 cm^{-1} are associated with different deformation modes of CH_2 groups [24]. The band at 1702 cm^{-1} can be associated with vibrations of C=C in olefinic compounds and the CH stretching bands are found at 2932 and 2856 cm^{-1} [25]. The 2363 and 2341 cm^{-1} band is assigned to the v (N–N) band of the containing N-species adsorbed on active sites are found, in accordance with the previous work [26,27]. The new bands increase in intensity with time on stream. These results show that the silanol groups on the surface of spent samples take part in interactions with reactants, and some N-carbon containing species such as olefinic/aromatic compounds are formed in the structure of the catalytic sample. Further, the band at 1654 cm^{-1} can be associated with the Si–N bond-containing species [24], from which we can hypothesize that the silica surface OH shows a weak dehydrogenating power during the oxidation process as confirmed by the detected products such as aniline and phenol. In addition, the band at 1627 cm^{-1} can be due to the bending mode of physisorbed water [25].

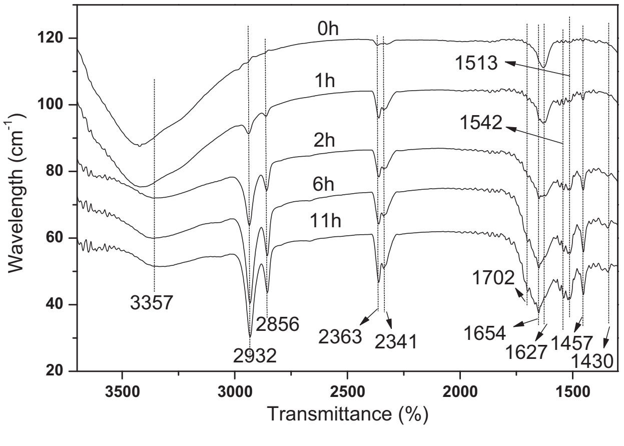
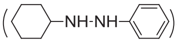


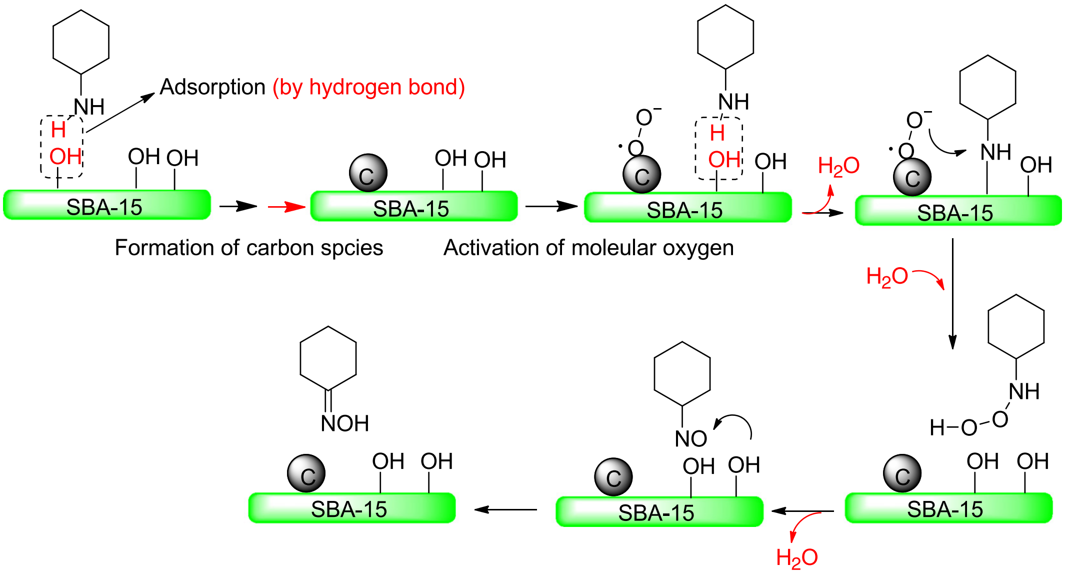
Fig. 3. The IR spectra of the fresh and spent samples.

The spent catalysts were dissolved in hydrofluoric acid, liberating retained hydrocarbons for extraction with CH_2Cl_2 and subsequent extract analysis by HPLC-MS. The composition and abundance of the retained hydrocarbon soluble in CH_2Cl_2 from the two spent catalysts are shown in Fig. S3. Based on the molecular mass of a given (molecular) ion, the most plausible structure diCHs (dimerized cyclohexylamine derivatives (), $m/z = 190.1$) are the main species, with amounts of triCHs ($m/z = 279.3$) and tetraCHs ($m/z = 354.3$), the corresponding trimer and tetramer cyclohexylamine derivatives observed in all spent samples, with the specific distributions of cyclohexyl-formed rings being different. Note that an increase in the extent of reaction is accompanied by redistribution between diCHs and triCHs: the fraction of diCHs in the products slightly drops, while the fraction of triCHs and tetraCHs increases. This redistribution is obviously caused by further polymerization reactions of the possible intermediate cyclohexylimine to triCHs, tetraCHs or pentaCHs on the SBA-15 surface, which also agrees with the results of the following elemental analyses. The analytical data of C, H and N percentages for the spent samples are shown in Table S1. The results indicated that carbon species formation increases with the time on stream. However, the composition of carbon species presented as an atom ratio C:H:N = 6:9:1 is almost constant, which corresponds to an empirical formula of $(C_6H_9N_1O_x)_n$. It was too difficult to get an accurate value for the percentage of O present.

The “formation of carbon species” pathway may therefore be operational on silica surfaces. Cyclohexylimine species may be formed via reaction of cyclohexamine with the surface OH groups, as was proposed by Dreoni et al. for silica under cyclohexamine atmosphere [24]. Cyclohexylimine species easily undergo oligomerization at reaction conditions. The silica catalyst was also active in dehydrogenation, resulting in formation of unsaturated/aromatic hydrocarbon deposits, in accordance with studies performed with other similar studies [28,29].

3.4. Proposed reaction pathway

On the basis of this observation, a reaction pathway of oxidation of the amine is proposed by following the next set of processes. First, cyclohexylamine should be adsorbed on the catalyst surface before oxidation (cyclohexylamine is not oxidized over dehydroxylated SBA-15). Subsequently, the autooxidation of cyclohexylamine adsorbed is initiated on the N–H group and forms carbon species, the carbon species can activate oxygen to produce the superoxide radial ion (O_2^-) on the surface of silica [16,30]. The adsorbed amine is rapidly activated by O_2^- to form the hydroperoxide as shown in the reaction (Scheme 1). Such hydroperoxide species in our system are decomposed rapidly to produce intermediate nitrosocyclohexane. Moreover, the nitroso derivative is isomerized to oxime.



Scheme 1. Mechanism of oxidation cyclohexylamine over the SBA-15 catalyst.

4. Conclusions

Mesoporous SBA-15 is an effective catalyst for the gas-phase oxidation of cyclohexylamine to oxime. The oxime selectivity reaches 96.6% at an amine conversion of 11.2%. The synergistic effect of the close contact between the carbon species formed on the surface and silanols is responsible for the excellent performance of SBA-15. In addition, the catalytic activity is also strongly dependent on the pore diameter of SBA-15.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 20976043)

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.06.030. This data include MOL files and InChiKeys of the most important compounds described in this article.

References

[1] G.M. Robertoson, in: A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), Comprehensive Functional Group Transformation, vol. 3, Elsevier, Oxford, 1995, pp. 425–441.
[2] H.-G. Liao, Y.-J. Xiao, H.-K. Zhang, P.-L. Liu, K.-Y. You, C. Wei, H. Luo, Catal. Commun. 19 (2012) 80–84.
[3] F. Cavani, N. Ballarini, S. Luciani, Top. Catal. 52 (2009) 935–947.
[4] J.S. Reddy, A. Sayari, Appl. Catal. A 128 (1995) 231–242.
[5] R. Joseph, T. Ravindranathan, A. Sudalai, Tetrahedron Lett. 36 (1995) 1903–1904.
[6] K. Suzuki, T. Watanabe, S.-I. Murahashi, Angew. Chem. Int. Ed. 47 (2008) 2079–2081.
[7] S.K. Klitgaard, K. Egeblad, U.V. Mentzel, A.G. Popov, T. Jensen, E. Taarning, I.S. Nielsen, C.H. Christensen, Green Chem. 10 (2008) 419–423.
[8] K. Rakottyay, A. Kaszonyi, Appl. Catal. A 367 (2009) 32–38.
[9] K. Rakottyay, A. Kaszonyi, S. Vajı´cˇek, Appl. Catal. A 378 (2010) 33–41.
[10] A. Bendandi, G. Fornasari, M. Guidoreni, L. Kubelkova, M. Lucarini, F. Trifiro, Top. Catal. 3 (1996) 337–354.
[11] A. Parmaliana, V. Sokolovski, D. Miceli, A. Mezzapica, F. Arena, N. Giordano, J. Catal. 148 (1994) 514–523.
[12] A. Satsuma, N. Sugiyama, Y. Kamiya, T. Hattori, Chem. Lett. (1997) 1051–1502.
[13] Y. Matsumura, K. Hashimoto, J.B. Moffat, J. Phys. Chem. 96 (1992) 10448–10449.
[14] H. Yoshida, T. Tanaka, M. Yamamoto, T. Funabiki, S. Yoshida, Chem. Commun. (1996) 2125–2126.
[15] T. Ono, M. Nakamura, K. Unno, A. Oyun, J. Ohnishi, M. Kataoka, K. Fujio, J. Mol. Catal. A 285 (2008) 169–175.
[16] Y. Barbaux, D. Bouqueniaux, G. Fornasari, F. Trifiro, Appl. Catal. A 125 (1995) 303–312.
[17] M.E. Davis, Nature 417 (2002) 813–821.
[18] M. Trejda, M. Ziolek, P. Decyk, D. Duczmal, Microporous Mesoporous Mater. 120 (2009) 214–220.
[19] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548–552.
[20] Y. Wang, M. Noguchi, Y. Takahashi, Y. Ohtsuka, Catal. Today 68 (2001) 3–9.
[21] T. Asefa, M.J. Maclachlan, N. Coombs, G.A. Ozin, Nature 402 (1999) 867–871.
[22] O.A. Anunziata, A.R. Beltramone, M.L. Martinez, L.L. Belon, J. Colloid Interface Sci. 315 (2007) 184–190.
[23] P.T. Tanev, M. Chibwe, T.J. Pinnavaia, Nature 368 (1994) 321–323.
[24] D.P. Dreoni, D. Dinelli, F. Trifiro, J. Mol. Catal. 71 (1992) 111–126.
[25] E.V. Starokon, M.V. Parfenov, S.S. Arzumanov, L.V. Pirutko, A.G. Stepanov, G.I. Panov, J. Catal. 300 (2013) 47–54.
[26] F. Wakabayashi, J. Kondo, A. Wada, K. Domen, C. Hirose, J. Phys. Chem. 97 (1993) 10761–10768.
[27] F. Wakabayashi, J.N. Kondo, K. Domen, C. Hirose, Microporous Mater. 8 (1997) 29–37.
[28] V. Ermini, E. Finocchio, A. Sechi, G. Busca, S. Rossini, Appl. Catal. A Gen. 190 (2000) 157.
[29] V.S. Sullivan, P.C. Stair, S.D. Jackson, in: S.D. Jackson, J.S.J. Hargreaves, D. Lennon (Eds.), Catalysis in Application, Proceedings of International Symposium on Applied Catalysis, 16–18 July 2003, Royal Society of Chemistry, Cambridge, 2003, p. 32.
[30] F. TrifirÒ, A. Vaccari, E. Giamello, G.F. Pedulli, Chem. Lett. 13 (1992) 21–26.